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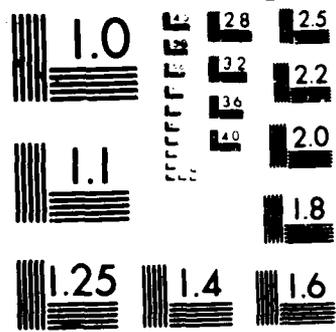
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MOLECULAR MOTION AND ENERGY MIGRATION IN POLYMERS

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The Royal Institution
London

Contract Number DAJA 37-82-C-0265

Second Periodic Report

January 1983 - June 1983

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In this phase of the work attention has been concentrated upon the technique of time-resolved fluorescence anisotropy, in which the time-dependence of the anisotropy r(t), defined below

$$r(t) = (I_{||}(t) - I_{\perp}(t))/I_{||}(t) + 2I_{\perp}(t)$$

$$= r_o \sum_i a_i \, e^{-t/\tau_i}$$

can in principle be used to monitor molecular motion. At the outset of this work, a study of the literature revealed many unsatisfactory features. There appeared to be no general agreement upon how properly to carry out the experiment, and interpretation was difficult. Much of the work described here consists of a critical evaluation of methods and applications to two polymers systems in solution, poly (methyl methacrylate) PMMA covalently labelled with poly (1-vinyl naphthalene) and poly (acenaphthylene) respectively, shown below. Anisotropy is a more useful parameter than degree of polarization in defining order and motion in molecular systems in that for a fluorophore which decays exponentially with a single component.

(Great Britain)
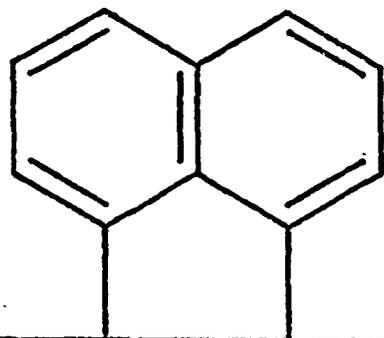
ACENAPHTHALENE LABELLED PMMA
("P/ACE")
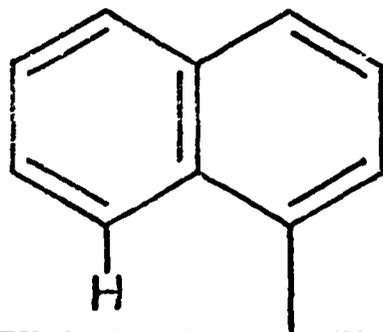
VINYLNAPHTHALENE LABELLED PMMA
("P/VIN")

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A-1

The resulting anisotropy constructed from independent measurements of the fluorescence parallel $I_\parallel(t)$ and perpendicular $I_\perp(t)$ to the plane of polarization of excitation radiation is <u>independent</u> of the decay time of the fluorophore. For systems which decay with dual (or more) components this is not necessarily the case, although it would be if the <u>motional</u>; properties of the two fluorophores giving rise to the two decay components were identical. Since there is not a prior way of ascertaining this, it seems prudent to employ fluorophores which are indeed single component. To assist in this a critical evaluation of the decay of standard substances which can be used to test single or dual exponentiality has been carried out [1].

Details of time-resolved anisotropy can also be obtained by deconvolution of individual $I_\parallel(t)$ or $I_\perp(t)$ measurements, or difference measurements defined below

$$I_\parallel(t) \qquad = \; e^{-t/\tau_F} \, (1 + 2r_o \, \sum_i a_i \, e^{-t/\tau_i})$$

$$I_\perp(t) \qquad = \; e^{-t/\tau_F} \, (1 - r_o \, \sum_i a_i \, e^{-t/\tau_i})$$

$$I_\parallel(t) - I_\perp(t) = 3r_o \, e^{-t/\tau_F} \, (r_o \, \sum_i a_i \, e^{-t/\tau_i})$$

In these cases analysis of $I_\parallel(t)$ and $I_\perp(t)$ are weighted, as usual, by Poisson statistics ($w_i = I_i^{-1}$). Fits of $I_\parallel - I_\perp$ and $r(t)$ must propogate these Poisson weightings into the proper fitting functions. Thus for

$$I_\parallel(t) - I_\perp(t), \quad w_i = (I_\parallel + I_\perp)^{-1}$$

and for $r(t)$, $w_i = 3(I_\parallel + 2I_\perp)/(2 + r + 5r^2 - 2r^3)$

These correct fitting are not universally employed in the literature, but are essential. Techniques are described in a chapter of a book of ours about to be published [2].

One advantage of using $I_\parallel(t)$ or $I_\perp(t)$ to extract anisotropy $r(t)$ is that analysis yields also a measure of τ_F which can be checked against values from independent 'magic angle' experiments. A disadvantage is that a two-component decay of anisotropy would result in the necessity for $I_\parallel(t)$ or $I_\perp(t)$ to be fitted by a three component model (since τ_F appears also), and the success and reliability of such a procedure is questionable. This point is demonstrated by the data in Table 1 for the poly (acenaphthylene) labelled PMMA in solution. From analysis of $I_\parallel(t)$ or $I_\perp(t)$ only one component of anisotropy can be reliably extracted, whereas upon analysis of the difference, $I_\parallel - I_\perp$, or anisotropy, two components are revealed. The second component is however questionable.

For PMMA - acenaphthylene in CH_2Cl_2 at 20° $\tau_r = 1.5 \pm 0.1$ ns, indicating rapid local motion of the polymer about the polymer backbone. Rather surprisingly, for PMMA - vinyl naphthalene, $\tau_r = 1.4 \pm 0.4$ ns. Because in this polymer the tag is attached to the backbone by only one bond, it would have been anticipated that depolarising motion would be more free, but the similarity of results in the two polymers indicates some unexpected restriction of rotation about the vinyl naphthalene/PMM bond.

This work is continuing. A preliminary report was given at the meeting on Polymer Photochemistry, Berlin, June 1983 (abstract enclosed,[3]).

Other anisotropy measurements have been made upon poly(styrene) labelled with phenyl oxazole PPO. It has been shown that for the direct excitation of the PPO label, decay of aniostropy on the time-scale of the fluorescence is observed (see Fig. 1). However, upon excitation of the styrene moiety with a mode-locked Ar^+ laser and observation of the PPO fluorescence, complete depolarization of the fluorescence is observed (Figure 2). While this observation does not necessarily support the proposition that multistep energy migration via styrene moieties is the mechanism of population of the PPO, it is consistent with this concept. These results conflict strongly however with the reports that polystyrene emission in solution is polarized. Further work is being carried out on this system. A preliminary report was given at the Berlin meeting (abstract included,[4]). Full reports of this work will be submitted for publication in the coming months, and will be included in the next periodic report.

2. The remainder of the contract will be spent carrying out the work specified in the proposal. Thus we will continue to investigate anisotropy in synthetic polymers, and have also begun recently to study the basic photophysics of dichromophoric model compounds for vinyl naphthalene polymers, viz 1,1 di-naphthyl propane, 2-2·dinaphthyl propane, and 1,2-dinaphthyl propane.

TABLE 1

A. COMPARISON OF DIFFERENT FITTING FUNCTIONS FOR P/ACE IN CH_2Cl_2 AT 20°C

FUNCTION	τ_f	τ_r	X_ν^2	FIT
$I_{\parallel}$	15.6 ns	1.39 ns	1.24	two exponentials
$I_{\perp}$	15.7	1.36	1.11	two exponentials
$I_{\parallel} + 2I_{\perp}$	15.6	-	1.21	one exponential
$I_{\parallel} - I_{\perp}$	-	1.20	1.45	one exponential
$I_{\parallel} - I_{\perp}$	-	0.29 1.77	1.08	two exponentials

FIGURE 1

ANISOTROPY PPO/POLYSTYRENE AT 300NM

TIME(NANOSECONDS)

ANISOTROPY*1000

AA:POLA.555
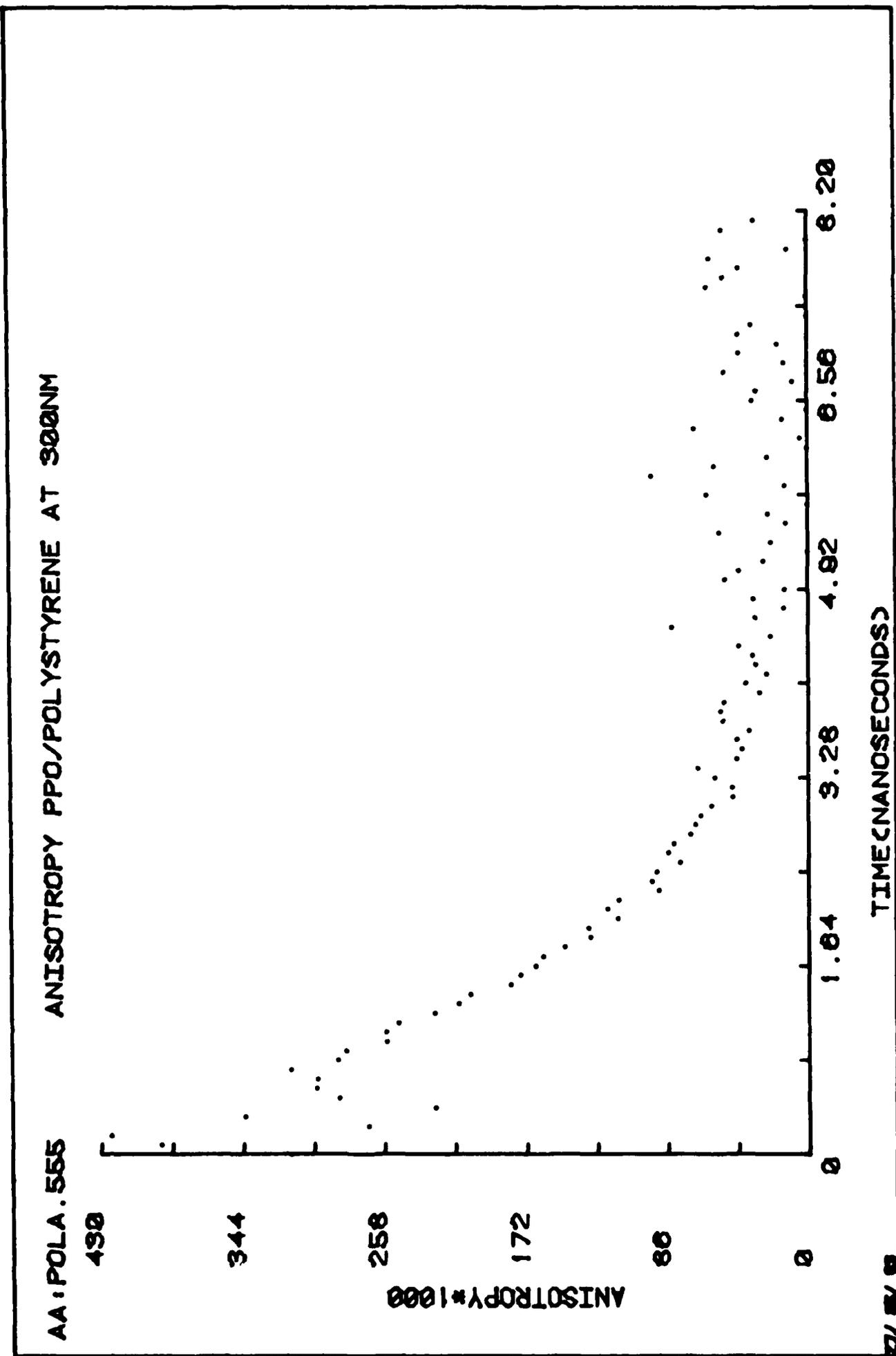
FIGURE 2

AA:PPOPARL.003

Parallel (pink) and perpendicular decays (blue) of PPO tagged polying
$I_{exc} = 257.25_{nm}$
$I_{em} = 405 \pm 5_{nm}$
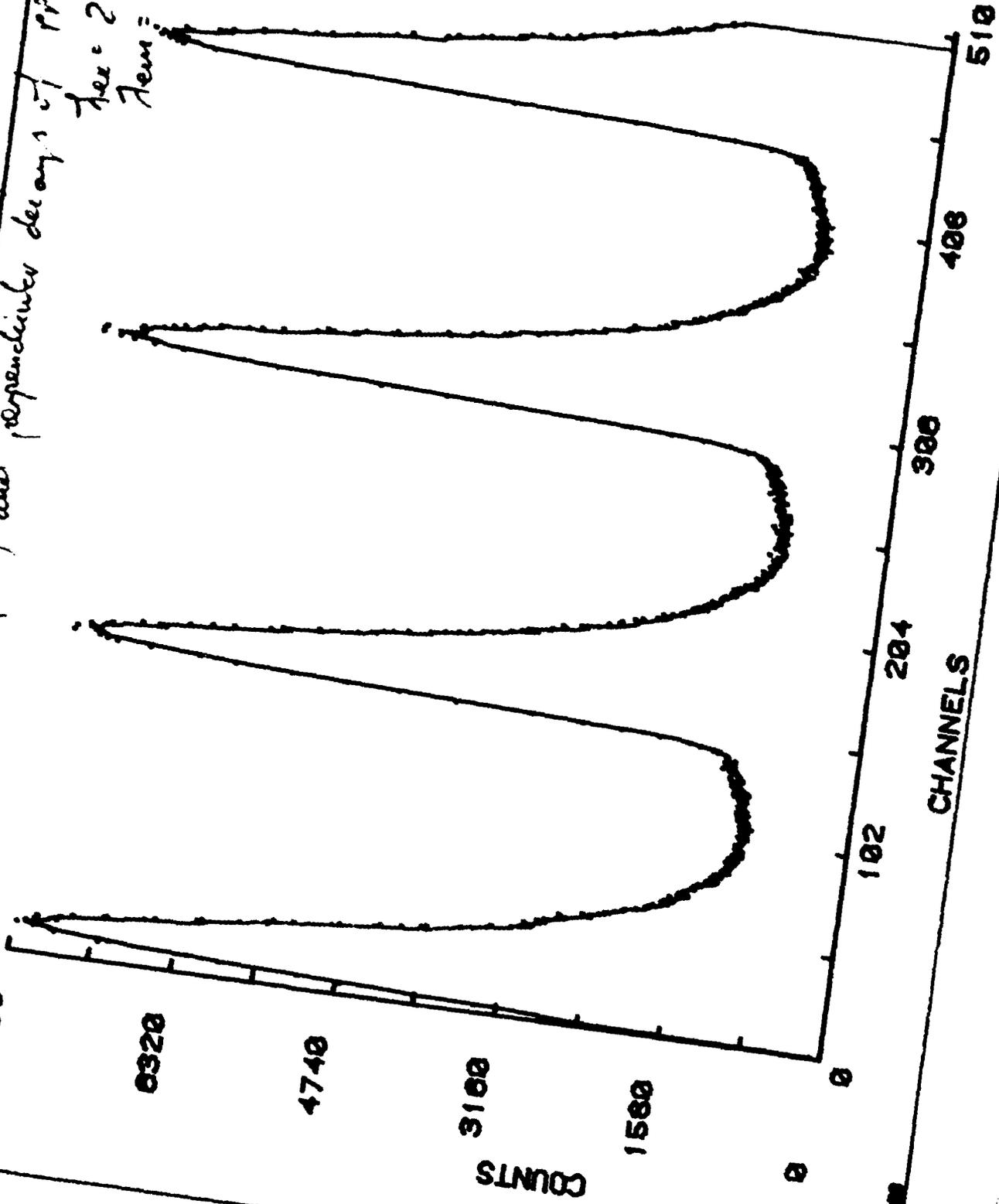
.. PPO EMISSION
COMPLETELY
DEPOLARIZED.

CHANNELS

COUNTS

Papers published or presented during Grant Period

1. "Standards for nanosecond fluorescence decay time measurements"
    R.A. Lampert, L.A. Chewter, D. Phillips, D.V. O'Connor, A.J. Roberts
    and S.R. Meech
    Analytical Chemistry 1983, 55, 68

2. "Time-correlated single-photon counting"
    D.V. O'Connor and D. Phillips
    Academic Press (in press) Chapter 8 "Time-dependence of
    fluorescence anisotropy."

3. "Time-resolved fluorescence anisotropy measurements on poly(vinyl
    aromatic) polymers"
    R.C. Drake, R.L. Christensen and D. Phillips
    Paper presented at International Conference on Polymer Photochemistry,
    Berlin June 1983.

4. "Excimer formation and energy transfer in vinyl aromatic polymers"
    David Phillips
    Paper presented at International Conference on Polymer Photochemistry,
    Berlin June 1983.

3.   The principal investigator attended the International Conference on Polymer Photochemistry, Berlin, June 1983, lecturing on the subject of this research. There have been no significant changes in personnel or in the direction of the work.

Annex

5(a)   The balance of unused funds remaining on the contract at the
        end of June 1983 is UC $43,166

 (b)   Funds were expended upon partial salary for Professor R.
        Christensen, computational facilities, materials, refrigerants,
        and replacement electronics.

END

Feb.

1988

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